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Amino acids/NH_3 mixtures for CO_2 capture: Effect of neutralization methods on CO_2 mass transfer and NH_3 vapour loss

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Abstract

Amino acid salts are effective promoters to improve CO_2 absorption in NH_3–based solutions, but at the expense of an increase in NH_3 vapour loss. To address this issue, we proposed the neutralisation of amino acids using NH_3 instead of KOH and investigated the effect of neutralisation methods on NH_3 vapour loss and mass transfer coefficient of CO_2 in amino acids/NH_3 mixtures at 15°C. It has been found that NH_3 neutralized amino acids solutions can enhance K_G of CO_2 in the NH_3 solution and suppress NH_3 loss at the same time. Among three amino acids investigated, taurine is most suitable for the NH_3 neutralisation. We developed the chemical equilibrium model for amino acid–NH_3–CO_2–H_2O and used the model to predict the species profiles in the mixture and explain the experimental results.

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Keywords: NH_3 neutralized amino acids solutions; NH_3 vapour loss; K_G of CO_2 ; chemical equilibrium model

1. Introduction

Post combustion capture (PCC) with aqueous amine solutions is a commercially available technology for significant reduction of CO_2 emissions from the fossil fuel based power plants and other industrial sources. However, the amines based PCC technologies are energy intensive and involve high capital and running costs [1]. In the presence of O_2, SO_2 and NO_x in the flue gas, amines undergo thermal and oxidative degradation, generating

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harmful side products and requiring solvent make up [2]. Therefore, research efforts have been intensifying aimed at the development of new solvent systems to reduce the capital and running costs of the PCC technologies.

Aqueous ammonia (NH_3) has been recognized as a promising alternative to amine–based absorbents for CO_2 capture since it is a low cost solvent, and has a high CO_2 absorption capacity and a low regeneration energy. Moreover, it does not degrade and is less corrosive to the absorber and stripper system. It also has a great potential of capturing multiple flue gas components (NO_x, SO_x and CO_2) and producing value added chemicals [3]. However, the NH_3–based capture processes face two major challenges [4]: low absorption rate for CO_2 capture which leads to a high capital cost and high vapour pressure of NH_3 which results in high NH_3 loss and hence leads to secondary environmental problems. To improve the performance of NH_3 for capturing CO_2, introduction of additives has been proved to be an effective way to improve CO_2 absorption rate in NH_3 solution. Amino acids are outstanding among all of studied additives, since they are low–cost, environmentally friendly, have lower vapour pressure and are less sensitive to oxygen than amines and have high reaction rates with CO_2 [5].

In aqueous solutions, amino acids can exist in three forms: protonated acidic form, neutral form, or deprotonated base form. Since only the deprotonated base form can react with CO_2, amino acids have to be neutralized by an equimolar amount of strong base, such as potassium hydroxide. In our previous work [6, 7], we investigated the effect of amino acid salts as additives on K_G of CO_2 absorption and NH_3 vapour loss in ammonia solution. We found addition of amino acid salts resulted in improvement of the overall mass transfer coefficient (K_G) of CO_2 absorption in ammonia solutions, but also significantly increased NH_3 vapour loss. The availability of more free NH_3 is one of main reasons for the increasing of NH_3 vapour loss. Based on our knowledge about NH_3 vapour loss, we proposed a hypothesis to use the weak base NH_3 to neutralize amino acids. By doing so, we expect that less free NH_3 is available in the NH_3 neutralised amino acid/NH_3 mixture and thus NH_3 vapour loss will be lower. To verify this hypothesis, we selected three amino acids (sarcosine, proline and taurine) and investigated K_G of CO_2 absorption and NH_3 vapour loss in NH_3 neutralized amino acids/NH_3 mixtures (no other base other than NH_3 was introduced into these solutions) and compared the results with those in strong base neutralized amino acids/NH_3 mixtures (amino acids were neutralized with an equal mole of KOH). We employed the reaction scheme for the amino acids–NH_3–CO_2–H_2O to predict species distribution in KOH neutralized or NH_3 neutralized amino acids/NH_3 mixtures and explain the experimental observations. The objectives of this paper is to understand the effect of neutralization methods on K_G of CO_2 absorption and NH_3 vapour loss and develop a new idea for amino acids promoted aqueous NH_3–based PCC processes.

2. Experimental

2.1 Chemicals

Analytic grade aqueous NH_3 with a weight concentration range of 25%–30% was purchased from Scharlau, and the exact NH_3 concentration was determined by titration using standard HCl (0.1 M solution, Fluka) with a titrator (Mettler Toledo T50). Potassium hydroxide (KOH, 85.9%) and ammonium bicarbonate (98%) were bought from VWR, Australia. Amino acids including sarcosine (98%), proline (99%) and taurine (99%) were bought from Sigma–Aldrich. Phosphoric acid was obtained from Chemsupply. Gases N_2 (99.95%) and CO_2 (99.5%) were supplied by BOC, Australia.

2.2 Solution preparation

The NH_3 neutralized amino acids/NH_3 mixtures were prepared by mixing the amino acids, NH_3 and distilled water directly. For KOH neutralized amino acids/NH_3 mixtures, the amino acids were neutralized with an equimolar amount of KOH to generate active base form first (amino acid salt) and then mixed with NH_3 and distilled water. CO_2–loaded mixtures were prepared by mixing the NH_3 solutions, ammonium bicarbonate and amino acids or amino acid salts. CO_2 loading in amino acids/NH_3 mixtures is defined as molar ratio of CO_2 to total alkalinity. Table 1 lists the KOH neutralized and NH_3 neutralized amino acids/NH_3 mixtures investigated in this work.

Table 1. Summary of NH_3–based solutions tested.

Solution	Condition
KOH neutralized amino acids/NH_3 mixtures	3M NH_3 + 0.3, 0.5, 1, 2, 3M sarcosine 3M NH_3 + 0.3, 0.6, 1, 2M proline/taurine;
KOH neutralized amino acids/NH_3 mixtures	3M NH_3 + 2M taurine; CO_2 loading (mol CO_2/mol alkalinity)=0, 0.1, 0.3, 0.5
NH_3 neutralized amino acids/NH_3 mixtures	3M NH_3 + 0.3, 0.5, 1, 2, 3M sarcosine 3M NH_3 + 0.3, 0.6, 1, 2M proline/taurine;
NH_3 neutralized amino acids/NH_3 mixtures	3M NH_3 + 2M taurine； CO_2 loading (mol CO_2/mol alkalinity)=0, 0.1, 0.3

2.3 Methods

Wetted–wall column

K_G of CO_2 was used to evaluate the CO_2 absorption kinetics in the mixtures and obtained on a wetted–wall column (WWC) facility. Figure 1 shows a schematic diagram of the WWC facility. A detailed description of this setup has been reported in our previous work [8]. CO_2 concentration in the gas was measured with a Horiba gas analyser. The NH_3 concentration in the gas at the outlet of the WWC was measured by a FTIR Analyzer DX4000 from Gasmet technologies. Since the NH_3 measurement range on FTIR is up to 10,000 ppm, a dilution gas N_2 was mixed with the gas leaving the WWC to reduce the NH_3 concentration below 10,000 ppm. The actual NH_3 concentration was calculated based on the flow rates of dilution gas and the gas mixture from the WWC.

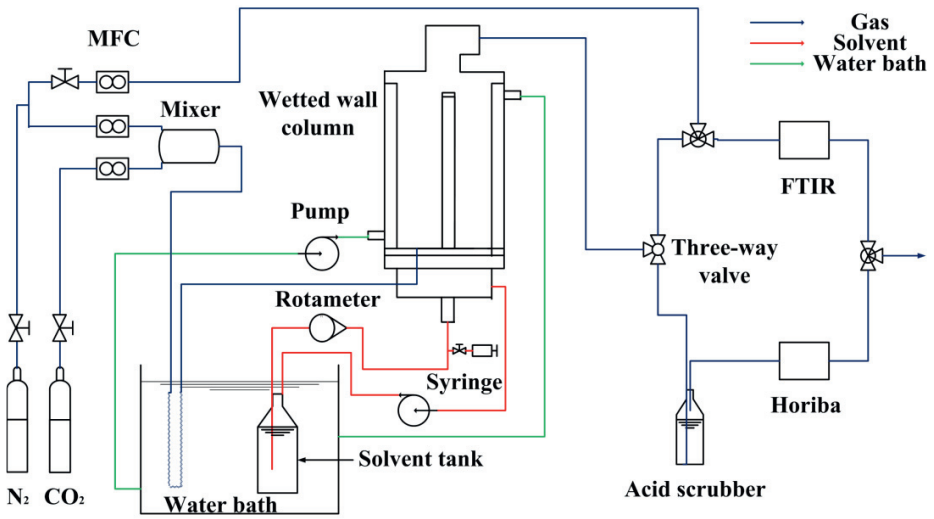

Figure 1. Schematic diagram of the wetted–wall column.

All tests were performed at the temperature of 15°C and a gas flow rate of 5 L/min. The solvent flow rate was kept at 100–120 ml/min to produce a laminar and ripple–free flow.

Chemical equilibrium model

Recently we have developed the reaction schemes of sarcosinate/prolinate/taurinate–NH_3–CO_2–H_2O. We have also confirmed that the mechanism of the reaction of CO_2 with the NH_3/sarcosinate blended solution is the simple combination of the individual reactions of NH_3 and sarcosinate with CO_2. Based on these works, we have developed chemical equilibrium and kinetic models for the systems of amino acid salts (sarcosinate/prolinate/taurinate)–NH_3–CO_2–H_2O to simulate the speciation profiles in the mixtures at equilibrium or as a function of reaction time. For example, Table 2 lists 10 reactions and the corresponding equilibrium constants in the chemical equilibrium model of taurinate–NH_3–CO_2–H_2O system. Three mass balance equations of the initial concentrations of CO_2, NH_3 and taurine and one charge balance equation of all species could be obtained. 14 equations were solved for 14 species including CO_3^{2-}, HCO_3^-, CO_2, H_2CO_3, NH_4^+, H^+, OH^-, NH_3, $NH_2CO_2^-$, NH_2CO_2H, $NH_2C_2H_4O_2SO^-$, $NH_3^+C_2H_4O_2SO^-$, $NH(CO_2^-)C_2H_4O_2SO^-$, and $NH(CO_2H)C_2H_4O_2SO^-$. A detailed description of model development has been reported in our previous work[7].

Table 2. Equilibrium reactions and their corresponding equilibrium constants at 15°C.

No.	Reactions	Equlibrium constants	References
1	$CO_3^{2-}+H^+ <=> HCO_3^-$	$K_1=2.69\times10^{10}$	Harned et al.[9]
2	$CO_2(aq) + H_2O <=> H_2CO_3$	$K_2=1.33\times10^{-3}$	Wang et al.[10]
3	$CO_2+H_2O <=> HCO_3^-+H^+$	$K_3=4.47\times10^{-7}$	Speight et al. [11]
4	$NH_3 + H^+ <=> NH_4^+$	$K_4= 3.56\times10^9$	Wang et al. [12]
5	$CO_2+NH_3 <=> NH_2CO_2H$	$K_5=7$	Wang et al. [12]
6	$NH_2CO_2^- + H^+ <=> NH_2CO_2H$	$K_6=5.5\times10^6$	Wang et al. [12]
7	$NH_2C_2H_4O_2SO^- + H^+ <=> NH_3^+C_2H_4O_2SO^-$	$K_7=2.04\times10^9$	Yang et al. [13]
8	$NH_2C_2H_4O_2SO^- + CO_2 <=>NH(CO_2H)C_2H_4O_2SO^-$	$K_8=6.85\times10$	Yang et al. [14]
9	$NH(CO_2^-)C_2H_4O_2SO^- +H^+ <=> NH(CO_2H)C_2H_4O_2SO^-$	$K_9=1.2\times10^7$	Yang et al. [14]
10	$OH^-+H^+ <=> H_2O$	$K_w=2.21\times10^{14}$	Maeda et al. [15]

3. Results and discussion

3.1 Effect of neutralization methods on K_G of CO_2 absorption and NH_3 vapour loss

Figure 2(a) and Figure 2(b) show measured NH_3 partial pressure at the gas outlet of wetted–wall column (can be treated as NH_3 vapour loss) and K_G of CO_2 as a function of concentration of amino acids in KOH neutralized and NH_3 neutralized amino acids/3M NH_3 mixtures at 15°C, respectively. NH_3 partial pressures in NH_3 neutralized amino acids/3M NH_3 mixtures were much lower than those in KOH neutralized amino acids/3M NH_3 mixtures. NH_3 partial pressures in NH_3 neutralized proline/3M NH_3 mixtures and in NH_3 neutralized sarcosine/3M NH_3 mixtures were relatively stable with increasing concentration of proline and sarcosine and similar to that in NH_3 alone solutions, while NH_3 partial pressure in NH_3 neutralized taurine/3M NH_3 mixtures decreased with an increase in concentration of taurine and was lower than that in NH_3 alone solutions.

Figure 2(b) illustrates that K_G of CO_2 in NH_3 neutralized amino acids/NH_3 mixtures was lower than that in KOH neutralized amino acids/NH_3 mixtures, but higher than that in NH_3 alone solution. K_G of CO_2 in NH_3 neutralized proline/NH_3 and sarcosine/NH_3 mixtures increased considerably initially with an increase in concentration of amino

acids but the extent of the increase became smaller when the concentration of amino acids increased close to 1M. The K_G of CO_2 in NH_3 neutralized proline/NH_3 mixtures was lower than that in NH_3 neutralized sarcosine/NH_3 mixtures. K_G of CO_2 in NH_3 neutralized taurine/NH_3 mixtures increased invariably with the increase of the concentration of taurine.

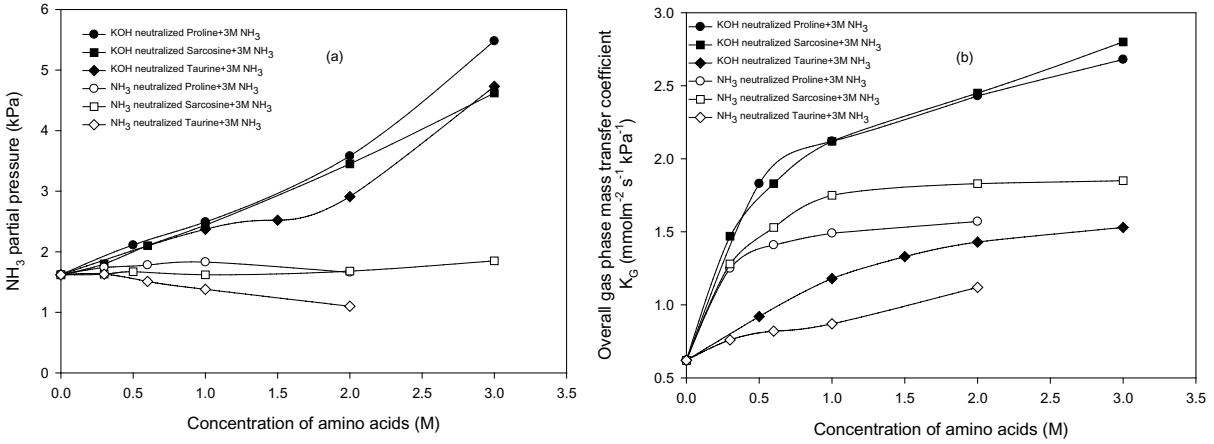

Figure 2. (a) NH_3 partial pressure at gas outlet of wetted–wall column; (b) K_G of CO_2 as a function of concentration of amino acids in different solutions at 15°C.

The chemical equilibrium model can help predict how much amino acids were neutralized by NH_3 in different NH_3 neutralized amino acids/NH_3 mixtures. According to the experimental condition in wetted–wall column study, we calculated the concentration profiles of active (basic form) proline, sarcosine and taurine and free NH_3 as a function of amino acid concentration in the mixtures at 15°C and present results in Figure 3.

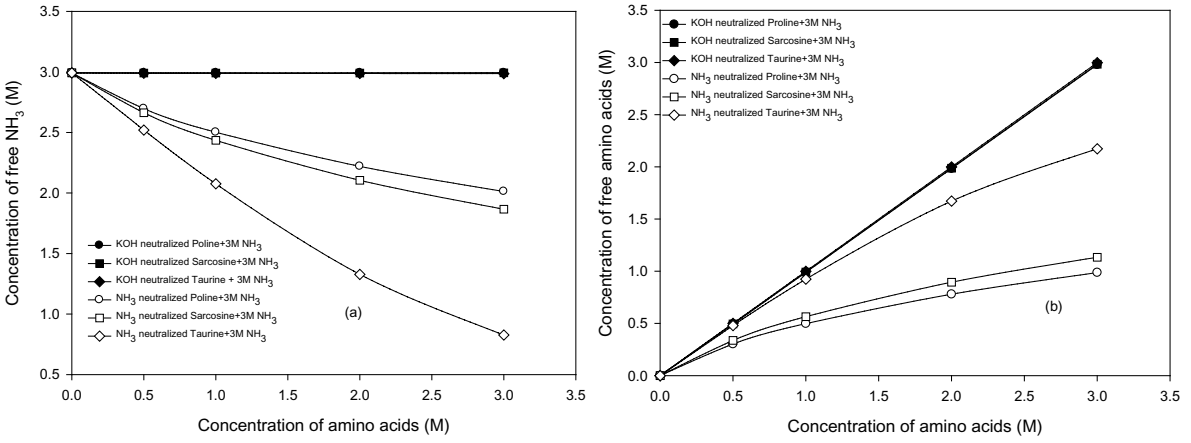

Figure 3. (a) Concentration of free NH_3; (b) Concentration of active (basic form) amino acids in different NH_3–based solutions as a function of concentration of amino acids at 15°C.

As shown in Figure 3(a), the concentration of free NH_3 in KOH neutralized amino acids/NH_3 mixtures was constant with an increase in concentration of amino acids, while the concentration of free NH_3 in NH_3 neutralized amino acids/NH_3 mixtures decreased with increasing concentration of amino acids. The concentration of free NH_3 in

NH_3 neutralized taurine/NH_3 mixtures were lower than that in NH_3 neutralized proline or sarcosine/NH_3 mixtures. Since the pKa values of three amino acids and NH_3 increase in the following order: taurine (9.31) < NH_3 (9.55) < sarcosine (10.51) < proline (10.67) at 15°C [12,13], taurine can be more easily neutralized by NH_3 than the other two amino acids. Corresponding to the concentration of free NH_3 in NH_3–based solutions as a function of concentration of amino acids, amino acids in KOH neutralized amino acids/NH_3 mixtures were completely converted to active amino acids. Only part of the amino acids in NH_3 neutralized amino acids/NH_3 mixtures could be neutralized by NH_3. The amount of active amino acids depended on their basicity, as shown in Figure 3(b).

The studies of the effect of neutralization methods on K_G of CO_2 absorption and NH_3 vapour loss show that, NH_3 neutralized amino acids solutions can enhance K_G of CO_2 in the NH_3 solution and suppress NH_3 vapour loss at the same time. Based on the prediction results from chemical equilibrium model, we found taurine can be neutralized readily, so it was selected for further investigation of the effect of CO_2 loading on K_G of CO_2 and NH_3 vapour loss in NH_3 neutralized taurine/NH_3 mixtures.

3.2 Effect of CO_2 loading on K_G of CO_2 absorption and NH_3 vapour loss

Figure 4(a) shows NH_3 partial pressure at the gas outlet of the wetted–wall column as a function of CO_2 loading in different solutions at 15°C. As shown in Figure 4(a), NH_3 partial pressures in all of solutions decreased with increasing CO_2 loading. NH_3 partial pressures in NH_3 neutralized taurine/3M NH_3 mixtures were lower than that in KOH neutralized taurine/3M NH_3 mixtures and even lower than that in 3M NH_3 alone solutions.

Figure 4(b) shows K_G of CO_2 in different solutions as a function of CO_2 loading at 15°C. As illustrated in Figure 4(b), K_G of CO_2 in different solutions decreased as CO_2 loading rose. K_G of CO_2 in NH_3 neutralized amino acids/NH_3 mixtures were higher than that in 3M NH_3 alone solutions. K_G of CO_2 in KOH neutralized taurine/NH_3 mixtures decreased dramatically, while K_G of CO_2 in NH_3 neutralized taurine/NH_3 mixtures decreased gradually. K_G of CO_2 in NH_3 neutralized taurine/NH_3 mixtures were similar to those in KOH neutralized taurine/NH_3 mixtures at CO_2 loadings between 0.1 to 0.3 (mol CO_2 /mol alkalinity).

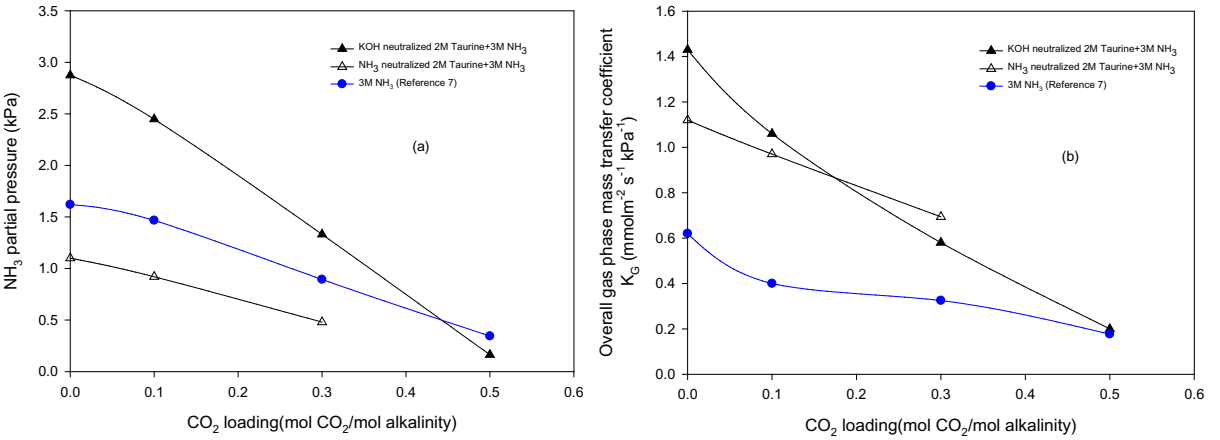

Figure 4. (a) NH_3 partial pressure at gas outlet of wetted–wall column; (b) K_G of CO_2 as a function of CO_2 loading in different NH_3–based solutions at 15°C.

Figure 5 shows the calculated concentration of free NH_3 and active taurine as a function of CO_2 loading in different NH_3–based solutions at 15°C. As expected, since part of NH_3 in NH_3 neutralized 2M taurine/3M NH_3 mixtures was consumed to neutralize taurine, free NH_3 in the NH_3 neutralized 2M taurine/3M NH_3 mixtures was lower than that in 3M NH_3, as shown in Figure 5(a). Figure 5(a) also illustrates that the amounts of free NH_3 were similar in KOH neutralized 2M taurine/3M NH_3 mixtures and 3M NH_3. However, our experimental results showed that, NH_3 vapour loss in KOH neutralized 2M taurine/3M NH_3 mixtures was higher than that in 3M NH_3. This

implies that other factors apart from the amount of free NH_3 affect the NH_3 vapour loss. As shown in our previous study [7], the solubility of CO_2 and NH_3 in the NH_3–based solutions and the competition for CO_2 between NH_3 and amino acids could also play a role in NH_3 loss. This requires further investigation.

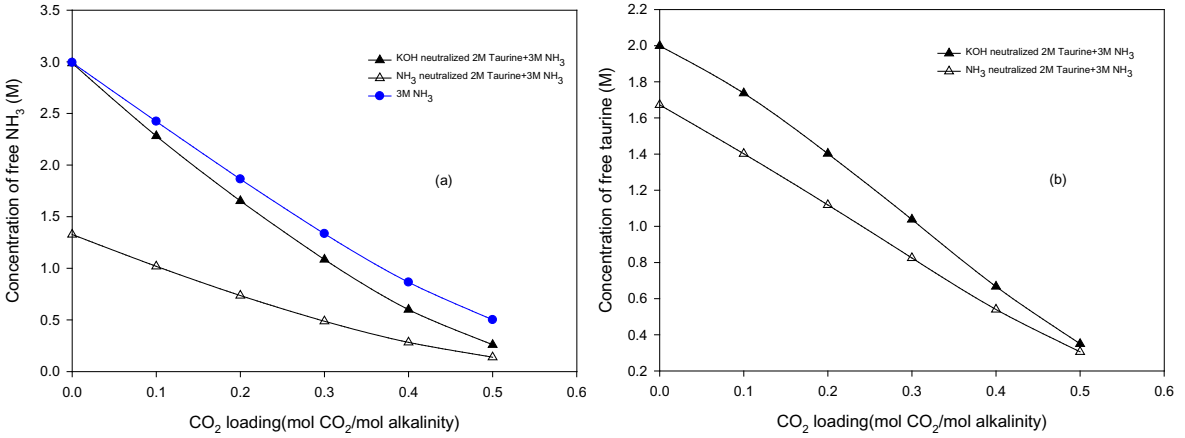

Figure 5. (a) Predicted concentration of free NH_3; (b) predicted concentration of active taurine in different NH_3–based solutions as a function of concentration of CO_2 loading at 15°C.

More free NH_3 and active taurine are present in KOH neutralized taurine/NH_3 mixtures than that in NH_3 neutralized taurine/NH_3 mixtures, as shown in Figure 5. So we expect that K_G of CO_2 in NH_3 neutralized taurine/NH_3 mixtures should be lower than that in KOH neutralized taurine/NH_3 mixtures. However it was not the case at CO_2 loading of 0.3. During the WWC experiments, the precipitation was observed. So it was possible that the formation of precipitation affected the measurement of K_G of CO_2. It needs to be pointed out that only the solution with the CO_2 loading less than 0.3 can be prepared for the measurements of NH_3 vapour loss and K_G of CO_2 at 15°C, due to the precipitation issue, but for the model prediction, we assumed no precipitate problem in the solution.

4 Conclusions

The effect of neutralisation methods on NH_3 vapour loss and K_G of CO_2 were investigated in amino acids/NH_3 mixtures at 15°C. It has been found that NH_3 neutralized amino acids/NH_3 mixtures can enhance K_G of CO_2 in the NH_3 solution and suppress NH_3 loss at the same time. Since the pKa values of taurine is lower than those of NH_3, most of taurine could be neutralized, so among three amino acids investigated, taurine is the most suitable for the NH_3 neutralisation. Compared to 3M NH_3 alone solution, NH_3 neutralized taurine/3M NH_3 mixtures had higher K_G of CO_2 and less NH_3 vapour loss. The chemical equilibrium models of amino acids–NH_3–CO_2–H_2O were used to predict the species profiles in the solutions to explain the experimental phenomenon. The precipitation occurred in NH_3 neutralized amino acids/NH_3 mixtures at high CO_2 loadings and needs to be addressed the in the future work.

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